PAPER PRODUCTS AND METHOD OF MAKING

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of our copending patent applications Serial Nos. 10/744,926 and 10/744,861 both entitled "Paper Products and methods of making" and filed December 22, 2003.

FIELD

The present invention is directed to printing paper, and to compositions and methods for making it.

BACKGROUND

Hardwood and softwood wood pulp fibers are used in the manufacture of printing paper and newsprint. These fibers are produced in a chemical pulping process, either sulfate or sulfite, or in a mechanical pulping process. Mechanical processes would include thermomechanical and chemithermomechanical. To form the printing paper or newsprint, these hardwood or softwood wood pulp fibers and wet end chemicals are mixed with water in the headbox of the paper machine to form a suspension of fibers and chemicals. The wet end chemicals may include fillers such as calcium carbonate and clay. Both of these chemical would have a mean average diameter of one micron or more. Other wet end chemicals would be internal sizes, opacifiers, brighteners, and dyes.

The suspension of fibers and chemicals flow from the headbox onto a wire. The water is removed from the fibers and chemicals by both gravity and vacuum to form a wet web of pulp fibers into which the chemicals are incorporated. The chemicals are throughout the sheet. The sheet may be pressed and/or dried to remove more water.

Starch, optical brightener additives and surface size may be placed on the surface of the sheet in a surface sizing step at the size press The materials that can be placed on the web at the size press must have a viscosity which allows the transfer of the material onto the web. Some of the materials may enter into the web if the pressure of the nip at the press is great enough.

Thereafter the web of fiber, wet end chemicals and other materials is dried by heat and calendered and rolled into rolls. The resulting product is referred to as an uncoated paper sheet or web.

The uncoated sheet is coated in another application of one or more coating layers placed on the sheet in an off-line coating operation. The uncoated sheet passes through a second coating station and a second drying station. This paper sheet or web is referred to as a coated paper sheet or web.

Uncoated or coated printing paper has a basis weight of from 16 to 180 pounds per 3300 square feet of paper.

The paper may be printed with either aqueous inks or thermal or toner inks. With either ink there is a concern about gloss variation and print variation of the ink, and the density of the ink on the paper. It is desired that the printing ink be evenly coated and have an even gloss. It is also desired that each of the different colored inks have an even density. It is also desired that the thermal toner adhere to the paper and not be easily removed.

In offset printing, ink from an ink roll is transferred to a printing plate. The printing plate has been treated so that ink is transferred to the plate in the printing regions of the plate and not transferred to the plate in the unprinted regions of the plate. The ink is transferred from the plate to a printing blanket which in turn transfers the ink to the paper. During the process of transferring ink from the blanket to the paper, fibers from the paper may attach and transfer to the blanket. This is called linting or picking. This is a problem because there is an unprinted section or void in the printed images following the transfer of the fiber to the blanket because no ink is transferred where the fiber is attached to the blanket. The standard solution to the void problem is to stop the printing press at intervals during the press run and clean the blanket to remove the fibers. Many size press formulations have been tried to prevent linting or picking. These formulations have provided limited improvement.

SUMMARY

In one embodiment the calcium carbonate has a mean particle size across the particle of 200 nanometers (nm) or less. In another embodiment the calcium carbonate has a mean particle size across the particle of 100 nm or less. In another embodiment the calcium carbonate has a mean particle size across the particle of 15 to 50 nm.

In one embodiment the small sized calcium carbonate can be placed on the web in amounts ranging from 0.1 to 300 pounds per ton of base paper. In another embodiment the small sized calcium carbonate can be placed on the web in amounts ranging from 5 to 150 pounds per ton of base paper. In another embodiment the small sized calcium carbonate would be placed on the web in amounts ranging from 15 to 80

pounds per ton of base paper. These weights would be divided between the two sides of paper. If the small sized calcium carbonate is applied to only one side of the sheet then the weights would be from 2.5 to 75 pounds per ton of base paper, or 7.5 to 40 pounds per ton of base paper, or up to 150 pound per ton of base paper.

In one embodiment of the invention the small sized calcium carbonate is applied at the size press or by a spray head before the dryer.

In another embodiment of the invention the small sized calcium carbonate is applied on an off-line coater.

In one embodiment the small sized calcium carbonate may be applied with a binder such as starch, modified starch or synthetic polymers or copolymers.

The attributes of the paper will depend on the use to which the paper is put.

In one embodiment of the invention a printing paper sheet or web having a small diameter calcium carbonate applied to its surface will have less linting or picking than a sheet that does not have such calcium carbonate on its surface. This will allow more impressions to be made before the press is stopped and the printing plate cleaned and reduces the cost and time of printing.

In another embodiment of the invention a printing paper sheet or web having a small diameter calcium carbonate applied to its surface will be stiffer than a sheet of the same weight that does not have such calcium carbonate on its surface. This will allow a sheet to be used where paper stiffness is required for post printing and conversion operations.

In one embodiment of the invention a printing paper sheet or web having a small diameter calcium carbonate applied to its surface will better toner adhesion than a sheet that does not have such calcium carbonate on its surface. The print will not be removed during use of the paper.

In another embodiment of the invention a printing paper sheet or web having a small diameter calcium carbonate applied to its surface will have less print variance than a sheet that does not have such calcium carbonate on its surface. The print will look better.

In another embodiment of the invention a printing paper sheet or web having a small diameter calcium carbonate applied to its surface will have less gloss variance than a sheet that does not have such calcium carbonate on its surface. The print will look better.

In another embodiment of the invention a printing paper sheet or web having a small diameter calcium carbonate applied to its surface will have better color density than a sheet that does not have such calcium carbonate on its surface. The print will look better.

In another embodiment of the invention an uncoated paper sheet or web having a small diameter calcium carbonate applied to its surface will have many of the attributes of a coated paper web or sheet that does not have such calcium carbonate on its surface. This will provide a less costly paper.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of a paper machine for uncoated paper.

Figure 2 is a schematic diagram of a paper machine for coated paper.

Figure 3 is a schematic cross sectional diagram of apparatus for obtaining a digital photograph for running the gloss variance and print variance tests.

Figure 4 is a schematic diagram of apparatus for obtaining a digital image used for the gloss variance values.

DETAILED DESCRIPTION

In one embodiment calcium carbonate having a mean particle size across the particle of 200 nm (0.2μm) or less is applied to the surface of a paper product. In another embodiment calcium carbonate having a mean particle size across the particle of 100 nm (0.1μm) or less is applied to the surface of a paper product. In another embodiment the calcium carbonate having a mean particle size across the particle of 15 nm (0.015μm) to 50 nm (0.05μm) is applied to the surface of a paper product. Throughout this application the term "small sized calcium carbonate" is used. The term refers to the above embodiments of calcium carbonate.

In one embodiment the small sized calcium carbonate is applied at the size press of a paper machine. It has been found that small sized calcium carbonate has the appropriate viscosity to be placed on the paper web at the size press. A portion of the small sized calcium carbonate may enter the web because of the nip pressure of the size press but much will remain on the surface of the web.

In another embodiment the small sized calcium carbonate can be sprayed on the web prior to the dryer. The majority of this material will remain on the surface of the web.

In one embodiment the small sized calcium carbonate can be placed on the web in amounts ranging from 0.1 to 300 pounds per ton of base paper. In another

embodiment the small sized calcium carbonate can be placed on the web in amounts ranging from 5 to 150 pounds per ton of base paper. In another embodiment the small sized calcium carbonate would be placed on the web in amounts ranging from 15 to 80 pounds per ton of base paper. These weights would be divided between the two sides of paper. If the small sized calcium carbonate is applied to only one side of the sheet then the weights would be from 2.5 to 75 pounds per ton of paper, or 7.5 to 40 pounds per ton of base paper, or up to 150 pound per ton of base paper.

In one embodiment the small sized calcium carbonate may be applied with a binder such as starch, modified starch or synthetic polymers or copolymers.

Figure 1 is a schematic drawing of a paper machine. Wood pulp fiber furnish and wet end chemicals are mixed with water in a headbox 10 to form a slurry. The slurry exits the headbox through a slice 12 onto a wire 14. The water in the slurry drains from the wire. A vacuum chest 16 is also used to draw water from the slurry to form a wet paper web. The web is carried through press rolls 18 and a drier 20 that remove additional water.

Additional size press chemicals or materials are placed on the wet paper web at the size press 22. The size press may be a horizontal type with the rolls horizontally aligned, or a vertical type with the rolls vertically aligned. The materials may be placed on the web from the rolls or from a puddle between the rolls. The web may, in some instances, be coated with material by the spraying apparatus 24. The materials described in the various embodiments in the present application would also be applied at the size press 22 or the spraying apparatus 24.

The paper web then passes through a drying section 26. The drying is usually done by steam heated drier cans through which the paper web is threaded. The paper is then calendered by calender rolls 28 and rolled into paper rolls at the winder 30. The resulting product is known as uncoated paper.

In the present invention the small sized calcium carbonate is added at the size press 22 or at the spraying apparatus 24. The resultant paper has better attributes than paper that is not coated with small sized calcium carbonate.

The small sized calcium carbonate, however, may also be placed on the paper web or sheet at the coating station of a machine for making coated paper.

Figure 2 is a schematic diagram of a paper machine for making coated paper. The reference numerals in Figure 1 and 2 are the same for the same elements. In Figure 2 there is an additional off machine coating operation. The web goes from the

dryer 26 to the coating operation and passes through a coating station 32. Coating station 32 is shown as rolls but any type of coating equipment may be used. The web may then pass through a dryer 34 and calender rolls 36. In some installations there are calender rolls before and after the coating station 32. The paper web is then wound into rolls 38.

The small sized calcium carbonate may be placed on the web at the coating station 32 instead of size press 22 or spray head 24. In some instances the small sized calcium carbonate may be placed on the web at the size press 22 or spray head 24 and the coating station 32.

In one embodiment the application of small sized calcium carbonate reduces the voids that are found in the print surface. The following test is used to determine this.

Void count test

The void count test was run using a Diddie offset web press. A printing plate having a solid printing area of approximately 12.6 in^2 is used. It has a 0.9 ink density and a uses a 40% screen. A void is an area which should be printed but is not printed. It is caused by fibers coming off the sheet surface and depositing on the printing plate or other printing surface and blocking further printing where it is deposited. This is called picking or linting.

A paper roll containing the equivalent of at least 6000 8 ½" x 11" paper sheets are run through the press using the same printing plate. The number of voids in the 12.6 in^2 solid printed area of the sheet are counted on the 1000th, 2000th, 4000th 6000th and 8000th sheet.

In another embodiment the application of small sized calcium carbonate increases the stiffness of paper. The following test is used to determine this.

Cross direction Gurley stiffness

Cross direction Gurley stiffness of a paper sheet is determined using Tappi test method T-543 om-94. The bending resistance of paper is determined by measuring the force required to bend a sample under controlled conditions.

Toner Adhesion Test. This test method is used to determine the toner adhesion of papers imaged on a Xerographic copy machine, folded and creased. A computerized image analysis is made of the crease in the solid image area. An average pixel width is calculated and converted to width in mm.

The equipment required for the test is a roller of specific weight and dimensions, cotton pads and a test sled.

The paper to be tested is conditioned at 50% relative humidity.

The copy machine is warmed up by running one ream of copy paper through the machine. 5% text is used.

A 5 block test pattern is used for the test. There is a pair of blocks at the top and a pair of blocks at the bottom of the test sheet. Each of the blocks is 3.8mm x 3.8mm. There is a single block at the center of the test sheet. This block is 3.8 mm x 7.5 mm. The copy machine is tested by printing 50 sheets with the test pattern and checking the density of the ink using a Gretag densitometer. The ink density should be between 1.50 and 1.54. If the density is in the target range of 1.50 to 1.54 then the samples can be printed. The samples should be in a 50% relative humidity environment during printing. The ink density should be monitored. If the density falls below 1.50 then printing of the sample sheets should be stopped. Additional copy paper should be printed until the density is above 1.50 and then printing of samples can be resumed.

The samples should be reconditioned at 50% relative humidity for 24 hours after printing.

A sample is folded in the machine direction so that a crease line will fall in the middle of the sample. The sample is gently pressed in the folded area without creasing the sample. The weighted roller is rolled gently over the folded area to create a crease. Use only the weight of the roller and a uniform and continuous movement in one direction to form the crease.

The paper is unfolded and a cotton pad is placed on the crease at one end of the crease. A sled having a weight of 305 grams is placed on top of the pad and both are pulled the entire length of the crease in one continuous motion. The other side of the pad is placed on the crease at the other end of the crease. The sled is placed on the pad and both are pulled along the crease I in the opposite direction.

A computerized image analysis is made of the crease in the solid image area. An average pixel width is calculated and converted to width in mm.

In the following examples, the small sized calcium carbonate was supplied by NanoMaterials Technology Pte Ltd (NMT). It is a precipitated calcium carbonate made using the high gravity reactive precipitation (HGRP) technology platform.

Example 1.

In this example, calcium carbonate having a mean size of 40 nm was applied to the surface of the paper with the use of starch (Penford Gum-290). Formulations were

made using 80-100 pounds ethylated starch (Penford Gum-290) per ton of paper and 0.5-180 pounds calcium carbonate per ton of paper. The amounts were pounds per ton based on the total weight of the paper and calcium carbonate. Two types of calcium carbonate were used. One was a standard coating grade of calcium carbonate having a mean averages diameter of 1 micron. The other was a calcium carbonate having a mean average diameter of 40 nm. The formulations were applied to a paper substrate using a laboratory two-roll press.

The substrate was a 70 pound per 3300 square feet paper web without size press starch and additives. The paper was prepared from a furnish including a blend of hardwood and softwood fibers and standard papermaking additives such as wet end starch, sizing, calcium carbonate, optical brighteners and retention aids.

Example 2.

The papers from Example 1 were tested for Gurley stiffness using TAPPI Method T543- om94. The results are summarized in Table 1.

Table 1

column	starch lbs/T paper	ethylated starch lbs/T paper	1 micron $CaCO_3$ lbs/T paper	40 nm $CaCO_3$ lbs/T paper	Cross-direction Gurley stiffness	Change over A %	Change over 1 micron %
A	80				119.1		
B		80	15		116.9		
		80		15	139.2	+16.8	+19.1
C		80	40		120.2		
		80		40	140.6	+18.1	+16.9
D		80	80		124.3		
		80		80	137.2	+15.2	+10.4
E		80	100		130.2		
		80		100	176.1	+47.9	+35.3
F		80	150		132.0		
		80		150	167.7	+40.8	+27

It can be seen that paper sheets coated with small sized calcium carbonate had an increase in cross-direction Gurley stiffness over the control sheet at even at low levels of application, and increased greatly at higher levels of application.. It can also be seen that small sized calcium carbonate had a higher cross-direction stiffness than conventional coating calcium carbonate at all levels of application.

Example 3.

In this example, calcium carbonate (NPCC-112) having a mean average size of 40 nm was applied to the surface of a paper web without the use of a binder such as starch, polyvinyl alcohol, or latex. Typically, a binder is required to attach calcium carbonate to the paper. The minimum ratio is 1 part binder to 1 part calcium carbonate.

The calcium carbonate was applied to the paper at 47 percent solids in a two-roll laboratory pond size press. The resulting paper had much of the calcium carbonate on its surface. The amount of calcium carbonate attached to the paper was at least 250 pounds per ton of paper.

Example 4.

Size press formulations were made using 40 pounds of ethylated starch (Penford Gum-290) per ton of paper per side. The formulations were applied to a paper substrate using a 2 roll size press and a gate roll.

The substrate was a 35 pound per 3300 square feet paper web without size press starch and additives. The paper was prepared from a furnish including a blend of hardwood and softwood fibers, and standard papermaking additives such as wet end starch, sizing, standard calcium carbonate, optical brighteners and retention aids.

Example 5.

Size press formulations were made using 80 pounds ethylated starch (Penford Gum-290) per 3300 square feet of paper per side of and two weights of calcium carbonate having a mean average size of 40 nm. The calcium carbonate weights were 20 pounds per 3300 square feet of paper per side and 40 pounds per 3300 square feet of paper per side. The formulations were applied to a paper substrate using a 2 roll size press.

The substrate was a 35 pound per 3300 square feet paper web without size press starch and additives. The paper was prepared from a furnish including a blend of hardwood and softwood fibers, and standard papermaking additives such as wet end starch, sizing, standard calcium carbonate, optical brighteners and retention aids.

Example 6.

Size press formulations were made using 80 pounds of ethylated starch (Penford Gum-290) per ton of paper per side. The formulations were applied to a paper substrate using a 2 roll pond size press.

The substrate was a 60 pound per 3300 square feet paper web without size press starch and additives. The paper was prepared from a furnish including a blend of

hardwood and softwood fibers, and standard papermaking additives such as wet end starch, sizing, standard calcium carbonate, optical brighteners and retention aids.

Example 7.

Size press formulations were made using 80 pounds of ethylated starch (Penford Gum-290) per ton of paper per side and various weights of calcium carbonate having a mean average size of 40 nm. The calcium carbonate weights were 7.5 pounds per ton of paper per side, 20 pounds per ton of paper per side, and 40 pounds per ton of paper per side. The formulations were applied to a paper substrate using a laboratory 2 roll pond size press.

The substrate was a 60 pound per 3300 square feet paper web without size press starch and additives. The paper was prepared from a furnish including a blend of hardwood and softwood fibers, and standard papermaking additives such as wet end starch, sizing, standard calcium carbonate, optical brighteners and retention aids.

Example 8.

The papers from example 4, 5, 6, and 7 were tested for void count and cross-machine Gurley stiffness. The results are summarized in Table 2.

Table 2

paper Lbs	starch lbs/T	small sized $CaCO_3$ lbs/T	Void 6K	Void 8K	Cross direction Gurley Stiffness mg
35	80		46.5		
35	80	40	4.0		
35	80	80	7.0		
60	80		47.0		127
60	80	15	15.0		138
60	80	40	7.0	10	165
60	80	80	12.0	13	172

It can be seen that void count was reduced with the application of small sized calcium carbonate. It can also be seen that cross machine Gurley stiffness increased.

Example 9.

In this example, calcium carbonate having a mean size of 40 nm was applied to the surface of the paper with the use of starch (Penford Gum-290). Formulations were made using 80 pounds ethylated starch (Penford Gum-290) per ton of paper and 0, 15, 40 or 80 pounds small sized calcium carbonate per ton of paper. The amounts were

pounds per ton based on the total weight of the paper and calcium carbonate. The starch and calcium carbonate were evenly divided on both sides of the paper. The formulations were applied to a paper substrate using a laboratory two-roll press.

The substrate was a 80 pound per 3300 square feet paper web without size press starch and additives. The paper was prepared from a furnish including a blend of hardwood and softwood fibers and standard papermaking additives such as wet end starch, sizing, calcium carbonate, optical brighteners and retention aids.

Example 10.

The samples from Example 9 were printed and tested using the toner adhesion test. The results are given in Table 3.

Table 3

paper Lbs	starch lbs/T	$CaCO_3$ lbs/T	Toner Adhesion Crack Width mm
60	80	–	0.521
60	80	15	0.280
60	80	40	0.247
60	80	80	0.248

Example 11

Figure 3 shows the cross section of an apparatus used to obtain prints which are used for the print variance values. Print variance is also known as print mottle. The device 20 creates diffuse illumination using an integrating sphere 22 onto which lights 24 shine. The diffuse light shines onto a flat surface 26 holding the sample 28 centrally of the sphere 22. A digital camera 30 is aligned perpendicular to the sample surface to capture a reflected light print image. A Kodak Megaplus digital area camera with a 52 mm lens was used in this example. The field of view for this evaluation is 51.2 x 51.2 mm. The full digital image is captured in a single frame as an area image. The light level is set by setting the camera F-stop and adjusting the shutter speed until the average pixel intensity is approximately 127.

Figure 4 shows an apparatus 40 used to obtain digital images which are used for the gloss variance values. Gloss variance is also known as gloss mottle. A sample 42 is placed onto a flat surface 44. The apparatus creates directional illumination using a light 46 oriented at an angle to the surface of sample 42. The directional light shines onto a flat surface of the sample 42. A digital camera 48 is on the side of the sample

42 opposite the light 46 and aligned with the light 46. The camera 48 captures the reflected light gloss image from the sample surface. The camera 48 is oriented at the same angle as light 46 so that the illumination and detection angles are equal. As an example, both the light 46 and camera 48 would be oriented at a 60° angle to the sample surface. An EG&G Reticon digital line camera with a 105 mm lens was used in this example. The field of view for this evaluation was 51.2 x 51.2 mm. The sample is moved linearly under convergence of the light beam and camera field so that the camera 48 captures individual lines which are reconstructed into an area image. The light level is set by setting the camera f-stop and adjusting the scanning speed until the average pixel intensity is approximately 120.

The images of the print and gloss samples are then used to determine print mottle and gloss mottle, respectively. The pixel intensity for each of the pixels on the photo is read and stored. If necessary, an 8 x 8 order polynomial regression is applied to the print images and a 1 x 4 polynomial regression is applied to the gloss images. The mean intensity for the entire regressed image is calculated. The mean intensity is subtracted from the individual regressed data to provide intensity difference image data. The intensity difference image data is multiplied by the pixel resolution in millimeters to scale the variance results. The autocovariance function of the intensity difference image data is calculated. The circular footprint Hanning window extending to the Nyquist frequency is also calculated. A windowed autocovariance function is calculated by multiplying the autocovariance function by the Hanning window extending to the Nyquist frequency. The full power density matrix is extimated from the windowed autocovariance function using a Fast Fourier Transform.

The image power is calculated by summing up the elements of the Fast Fourier Transform array. The image power is given in Table 4. The variance was better when small sized calcium carbonate was used.

Table 4

paper Lbs	starch lbs/T	$CaCO_3$ lbs/T	Gloss Var. Image Power	Print Var. Image Power.
60	80	–	4.17	0.190
60	80	15	3.40	0.135
60	80	40	3.08	0.150
60	80	80	2.72	0.160

Example 11.

Paper samples was printed with black, cyan, magenta and yellow using an HP 990C printer. The density of the colors was evaluated using a Gretag densitometer. The results are shown in Table 5. Density increased with increasing amounts of small sized calcium carbonate.

Table 5

paper Lbs	starch lbs/T	$CaCO_3$ lbs/T	HP 990C Gretag Densi. Black	HP 990C Gretag Densi. Cyan	HP 990C Gretag Densi. Magenta	HP 990C Gretag Densi. Yellow
60	80	–	1.04	1.01	0.89	0.75
60	80	15	1.42	1.02	0.97	0.76
60	80	40	1.35	1.06	1.01	0.78
60	80	80	1.36	1.09	1.05	0.81

Those skilled in the art will note that various changes may be made in the embodiments described herein without departing from the spirit and scope of the present invention.